Functionalization of Rhenium Aryl Bonds by O-Atom Transfer

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General Procedures: All manipulations were carried out using an argon filled MBraun glovebox and standard Schlenk techniques using over dried glassware (>1 h at 110 °C under vacuum, -30 mm Hg). THF was HPLC grade from EMD and distilled over Na/Benzophenone and then degassed under argon before use. H_2O was degassed and stored under argon before use. Pentane was HPLC grade from EMD and distilled over NaH prior to use. Reagent-grade chemicals and solvents were purchased from Sigma Aldrich, Alfa Aesar, or EMD and used as is unless otherwise specified. Deuterated solvents were purchased from Cambridge Isotope Inc. and degassed and stored under argon before use. Re_2O_7 was obtained from Strem or Alfa and stored in the glovebox freezer (-30 °C) before use. $H_2{}^{18}O_2$ was obtained from Sigma Aldrich. $H_2{}^{18}O$ was obtained from Cambridge Isotopes Inc. Elemental analyses were performed by Columbia Analytical Services; Tucson, Arizona. Electrospray Ionization (ESI) mass spectroscopy was performed at the University of Florida Mass Spec Facility; Gainesville, Florida. Liquid phase organic products were analyzed with a Shimadzu GC-MS QP2010S equipped with cross-linked methyl silicone gum capillary column, RTX-5. Gas measurements were performed using an Agilent GasPro column. The retention times of the products were confirmed by known standards. NMR spectra were obtained on a Bruker Digital Avance III 400 (400.132 MHz for ^{1}H and 100.623 MHz for ^{13}C) spectrometer. Chemical shifts are given in ppm relative to residual solvent proton resonances or to a stated internal or external standard. The rhenium phenyl, tolyl, pentafluoro, and mesityl trioxides have been previously prepared and characterization data of these compounds compared with that of previous reports.[1] The phenyl and pentafluoro diaryl-zincs were purchased from Strem Inc. The tolyl[2] and mesityl[3] diaryl-zincs were prepared as previously described.

Dimesityl Zinc(II) Synthesis:[4] The MesMgBr reagent is prepared by reaction of 8 g of Mg turnings and 50 g mesitylbromide in 200 mL of THF. After Addition of the mesitylbromide, the solution is heated for 1 h in a hot water bath (~75 °C). The solution is then cannula filtered to a new flask followed by the addition of 30 g of $ZnCl_2$ dissolved in 150 mL of THF to the stirred THF/Grignard solution by cannula. The mixture is stirred for 2 h at RT and 1 h at 50 °C before adding 20 g of dry dioxane drop wise to precipitate the remaining Mg salts. After separation of the precipitate, the solvent is removed and the residue is dissolved in diethylether and filtrated. Further purification is achieved by recrystallization from hot ether (Toluene was also found to work well for the recrystallization).

General Procedure for Oxidation of Re-Aryls: In an argon filled glovebox with the light off, a screw cap NMR tube with PTFE septa was loaded with ~15 μmol of respective $ReArylO_3$. The NMR tube also contained a coaxial, capillary, external standard loaded with a 56 mM solution of 1,3,5-trimethyoxybenzene in CD_3CN. To this solid, 0.6 mL of a 5:1 solution of THF-D_8:D_2O was added to the NMR tube. An initial ^1H NMR was taken. Then, 3 eq. of the respective oxidant was added (unless otherwise stated) and the NMR tube was then shaken and allowed to sit at RT for 1 h. The reaction was monitored by ^1H NMR before and after reaction. Yields were determined by comparison of both the aromatic and methyl proton integrations. Products were confirmed in ^1H and ^{13}C NMR by spiking with authentic samples. Products were also confirmed qualitatively by GC-MS analysis and comparison to authentic standards for retention time and fragmentation pattern.

Oxidation of $MesReO_3$ with H_2O_2 and confirmation of 2,4,6-trimethylphenol.

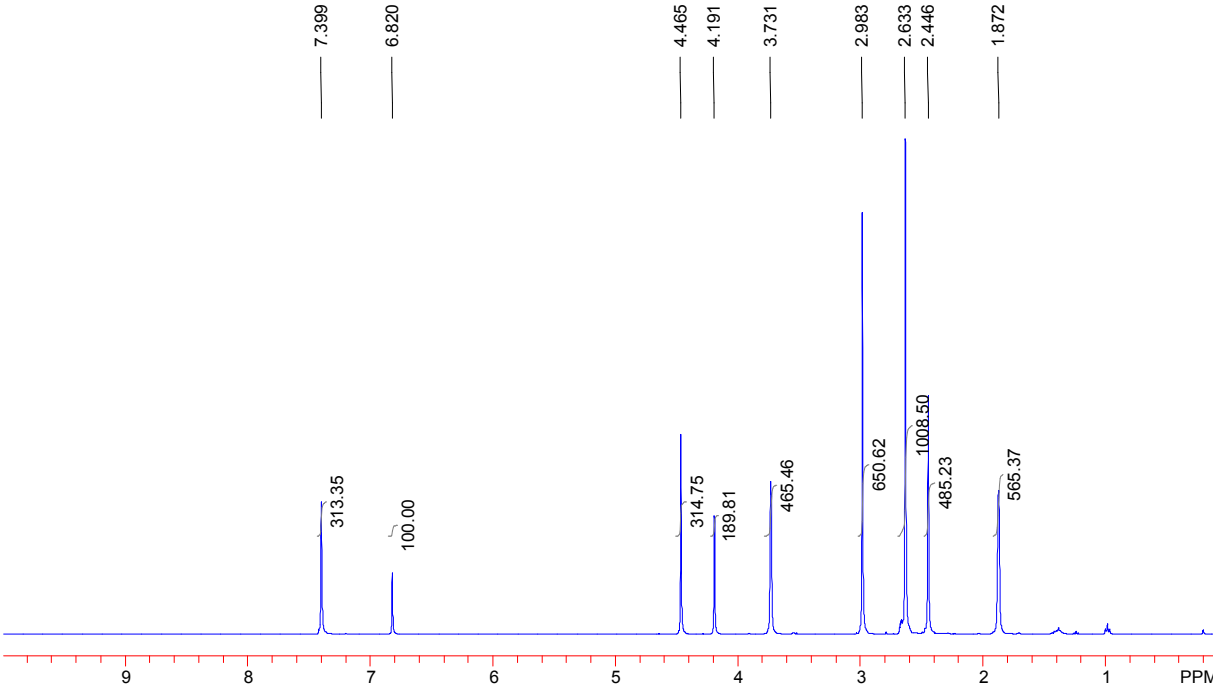


Figure S 1. ^1H NMR of $MesReO_3$ in 5:1 THF-D_8:D_2O at T = 0 h: δ 7.39, 2.63, and 2.44 ($MesReO_3$); 3.73 and 1.87 (residual protio THF); 6.82 and 4.46 (1,3,5-trimethoxybenzene from external standard); 4.19 (residual H_2O in solution); 2.98 (residual H_2O in external standard).

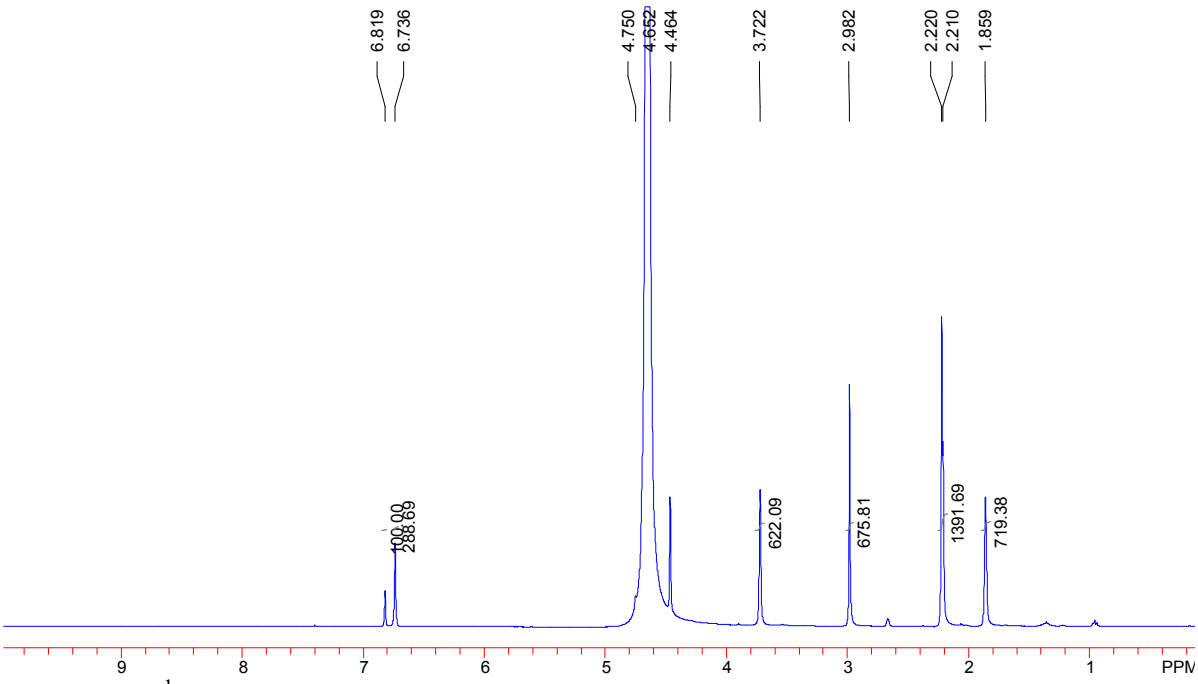


Figure S 2. ^1H NMR of $MesReO_3$ in 5:1 THF-D_8:D_2O at T = 10 min. following addition of 3eq of H_2O_2 at RT: δ 6.73, 2.22 and 2.21 (2,4,6-trimethylphenol); 3.72 and 1.85 (residual protio THF); 6.81 and 4.46 (1,3,5-trimethoxybenzene from external standard); 4.65 (residual protio H_2O in solution); 2.98 (residual H_2O in external standard).

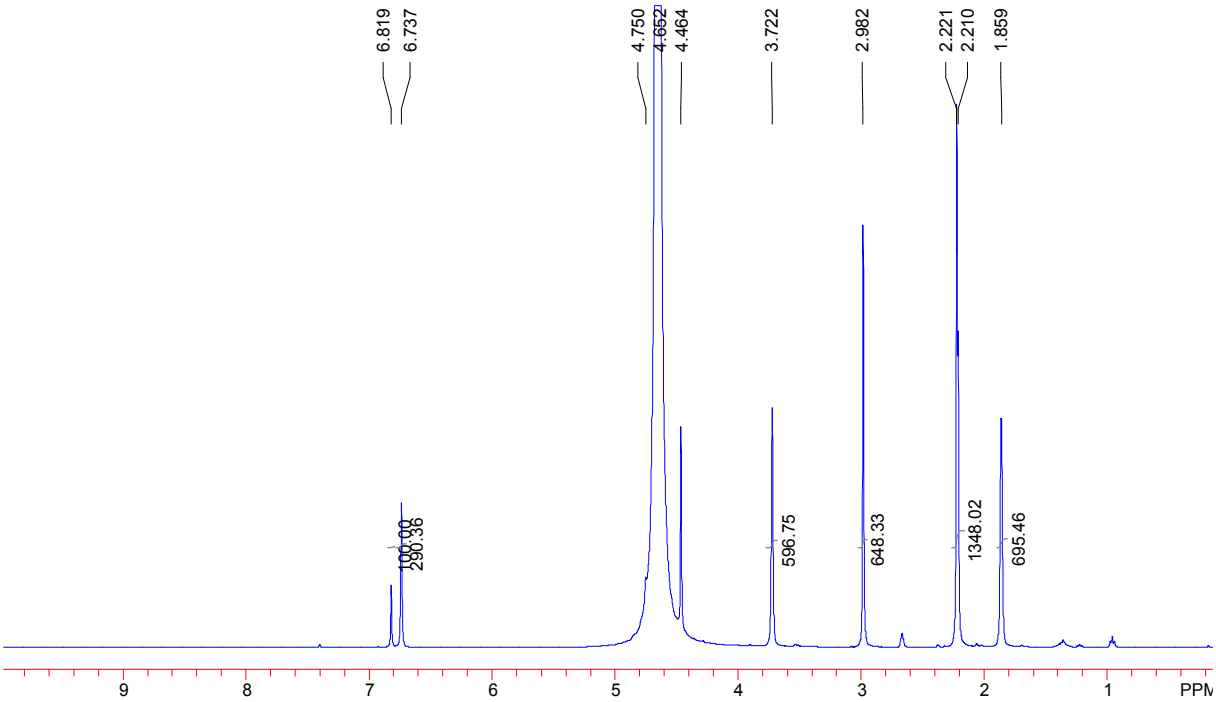


Figure S 3. ^{1}H NMR of $MesReO_3$ in 5:1 THF-D_8:D_2O at T = 1 h at RT: δ 6.73, 2.22 and 2.21 (2,4,6-trimethylphenol); 3.72 and 1.85 (residual protio THF); 6.81 and 4.46 (1,3,5-trimethoxybenzene from external standard); 4.65 (residual protio H_2O in solution); 2.98 (residual H_2O in external standard).

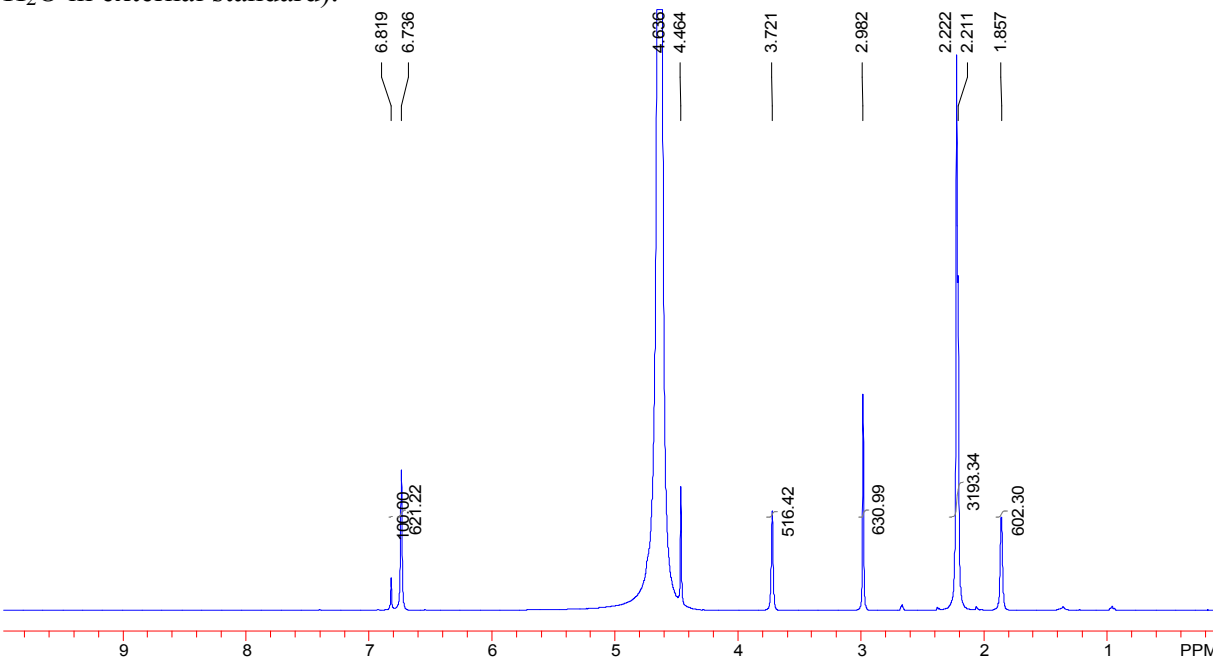


Figure S 4. ^{1}H NMR of $MesReO_3$ in 5:1 THF-D_8:D_2O at T = 2 h at RT spiked with 50uL of 2,4,6-trimethylphenol: δ 6.73, 2.22 and 2.21 (2,4,6-trimethylphenol); 3.72 and 1.85 (residual protio THF); 6.81 and 4.46 (1,3,5-trimethoxybenzene from external standard); 4.65 (residual protio H_2O in solution); 2.98 (residual H_2O in external standard).

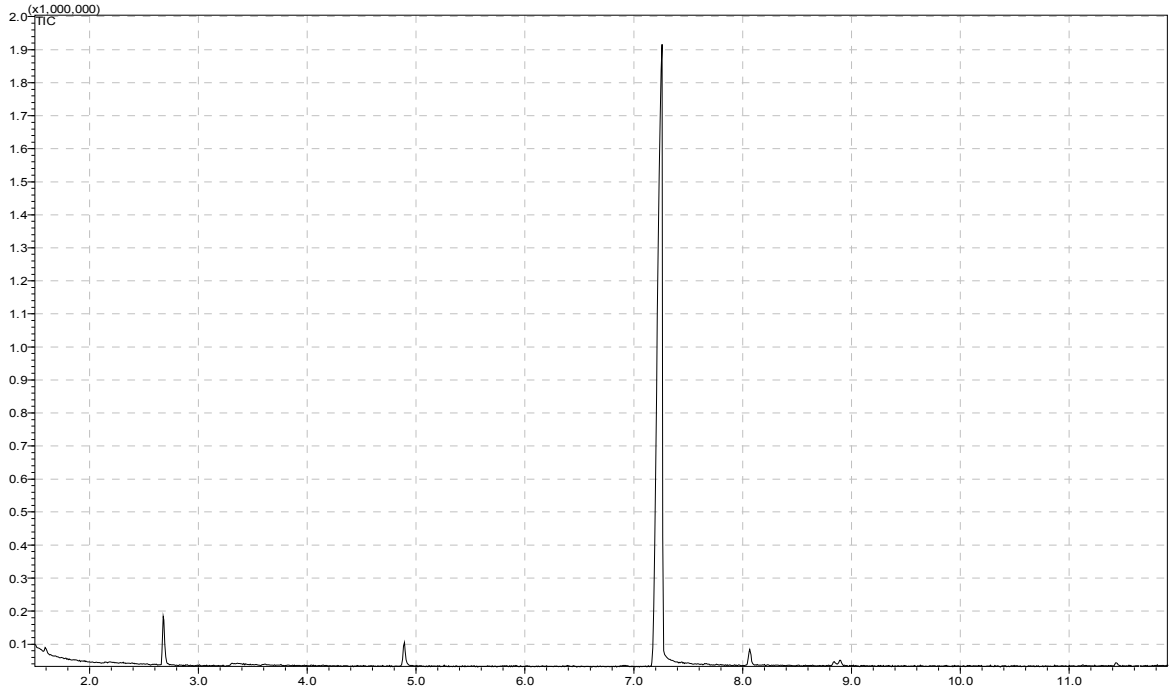


Figure S 5. GC chromatogram of an authentic sample of 2,4,6-trimethylphenol, T_r = 7.23 min, $[M]^+$ = 136, where the X-axis is Time (min) and the Y-axis Counts (in millions).

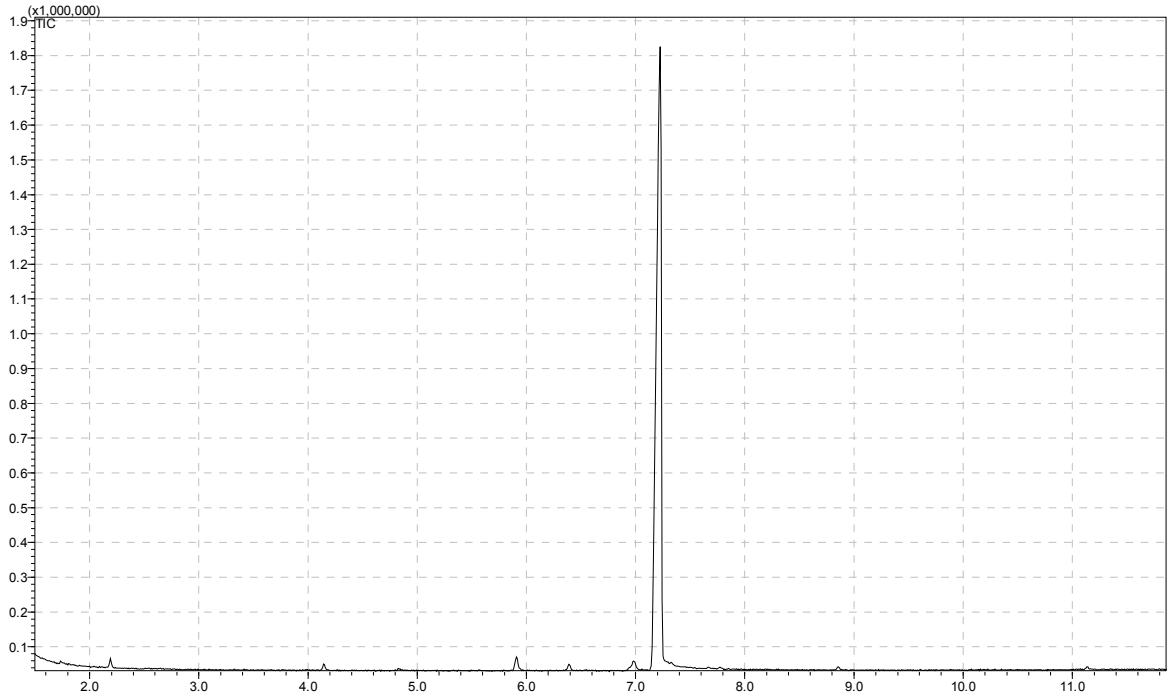


Figure S 6. GC chromatogram of the reaction between $MesReO_3$ and 3eq of H_2O_2 in 5:1 THF:H_2O, T_r = 7.22 min, $[M]^+$ = 136, where the X-axis is Time (min) and the Y-axis Counts (in millions).

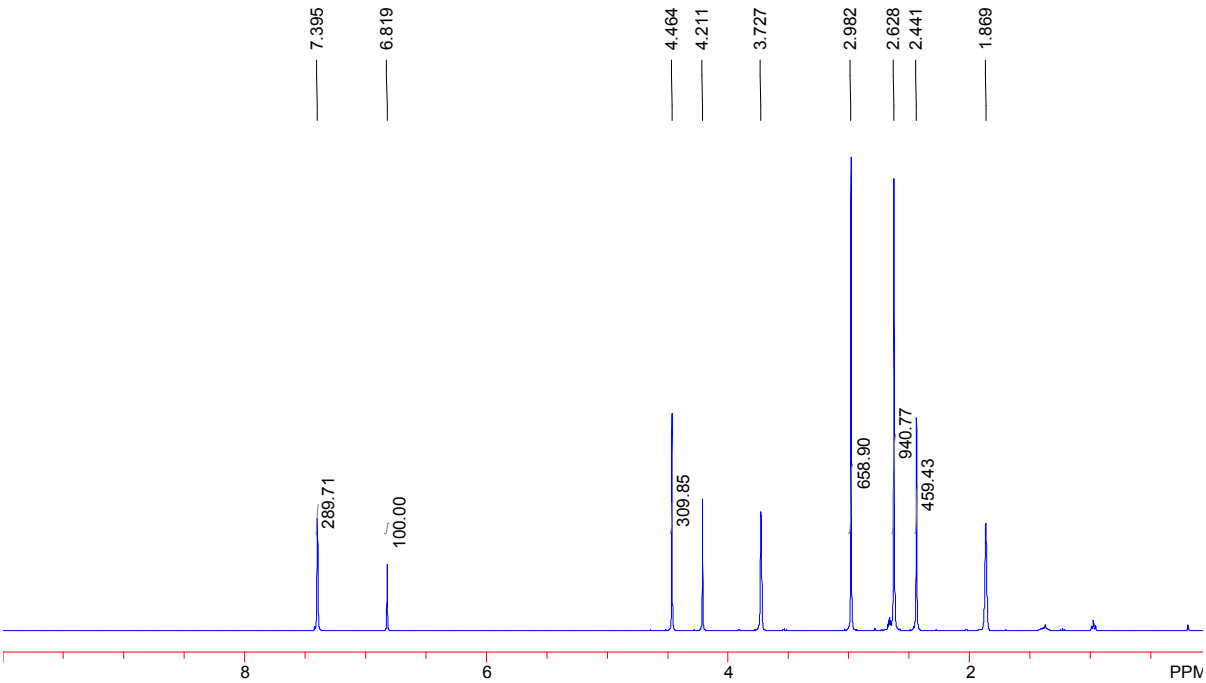


Figure S 7. ^{1}H NMR of $MesReO_3$ before $NaIO_4$ in 5:1 THF-D_8:D_2O at T = 0 h at RT: δ 7.39, 2.62, and 2.44 ($MesReO_3$); 3.72 and 1.86 (residual protio THF); 6.81 and 4.46 (1,3,5-trimethoxybenzene from external standard); 4.21 (residual H_2O in solution); 2.98 (residual H_2O in external standard).

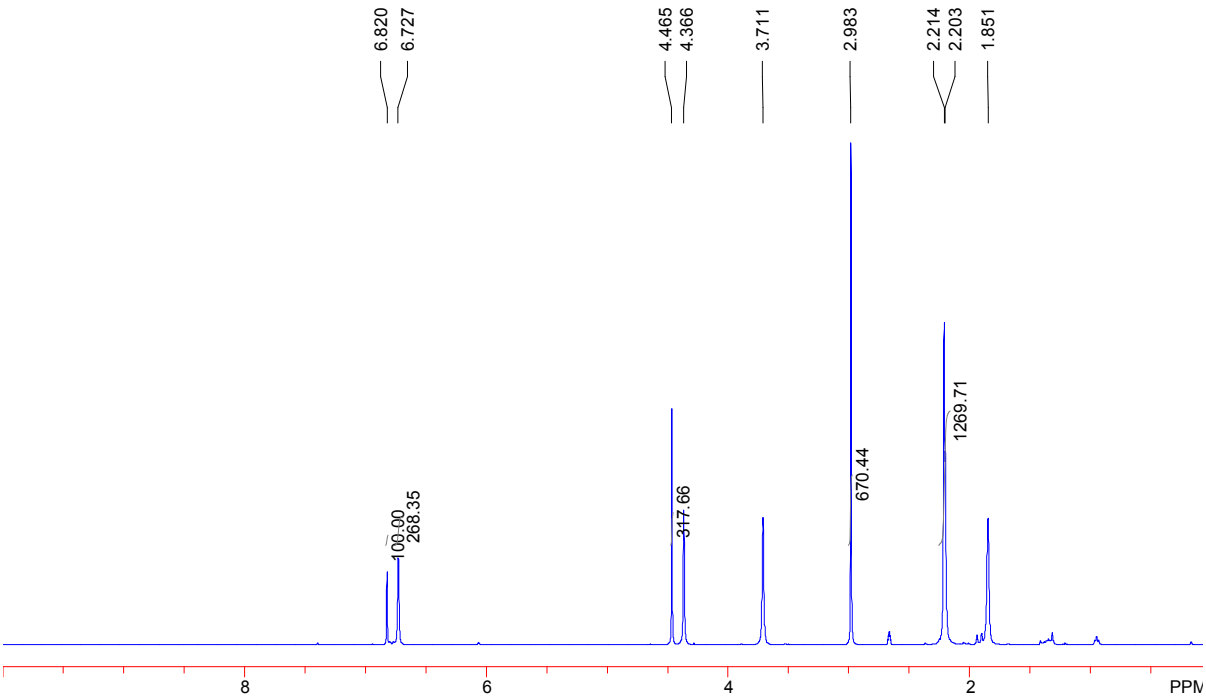


Figure S 8. ^{1}H NMR of $MesReO_3$ + $NaIO_4$ in 5:1 THF-D_8:D_2O at T = 1 h at RT showing formation of 2,4,6-trimethylphenol: δ 6.72, 2.21 and 2.20 (2,4,6-trimethylphenol); 3.71 and 1.85 (residual protio THF); 6.82 and 4.46 (1,3,5-trimethoxybenzene from external standard); 4.36 (residual protio H_2O in solution); 2.98 (residual H_2O in external standard).

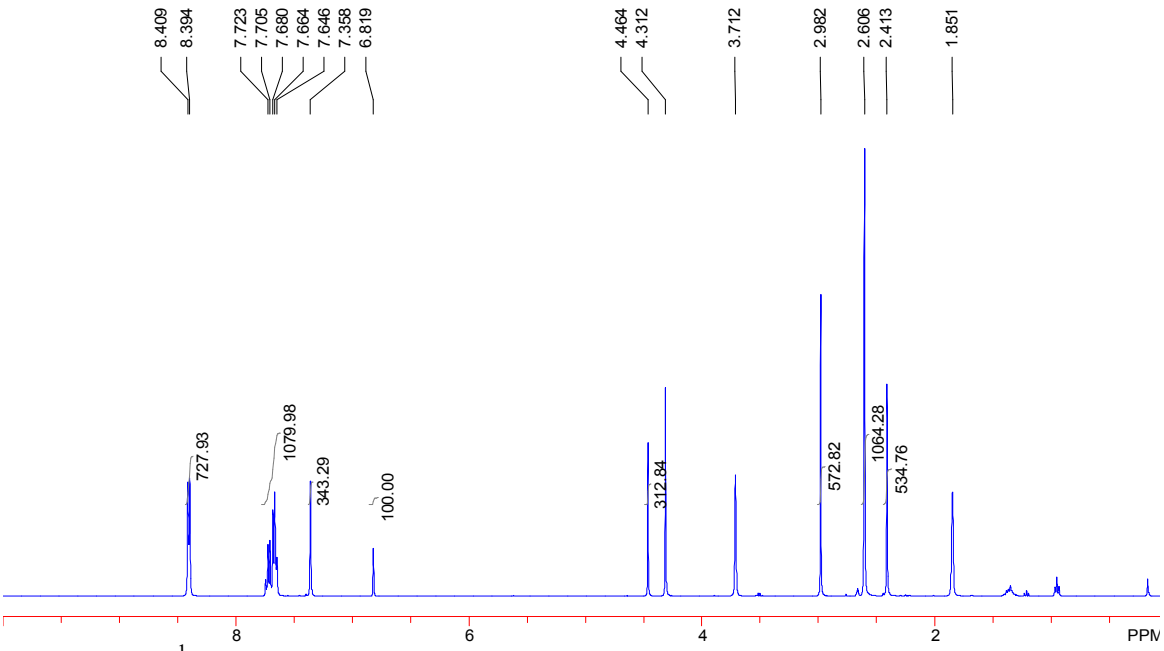


Figure S 9. ^{1}H NMR of $MesReO_3$ + PyNO in 5:1 THF-D_8:D_2O at T = 0 h: 8.40 and 7.05 (pyridine N-oxide); 7.35, 2.60, and 2.41 ($MesReO_3$); 3.71 and 1.85 (residual protio THF); 6.81 and 4.46 (1,3,5-trimethoxybenzene from external standard); 4.31 (residual protio H_2O in solution); 2.98 (residual H_2O in external standard).

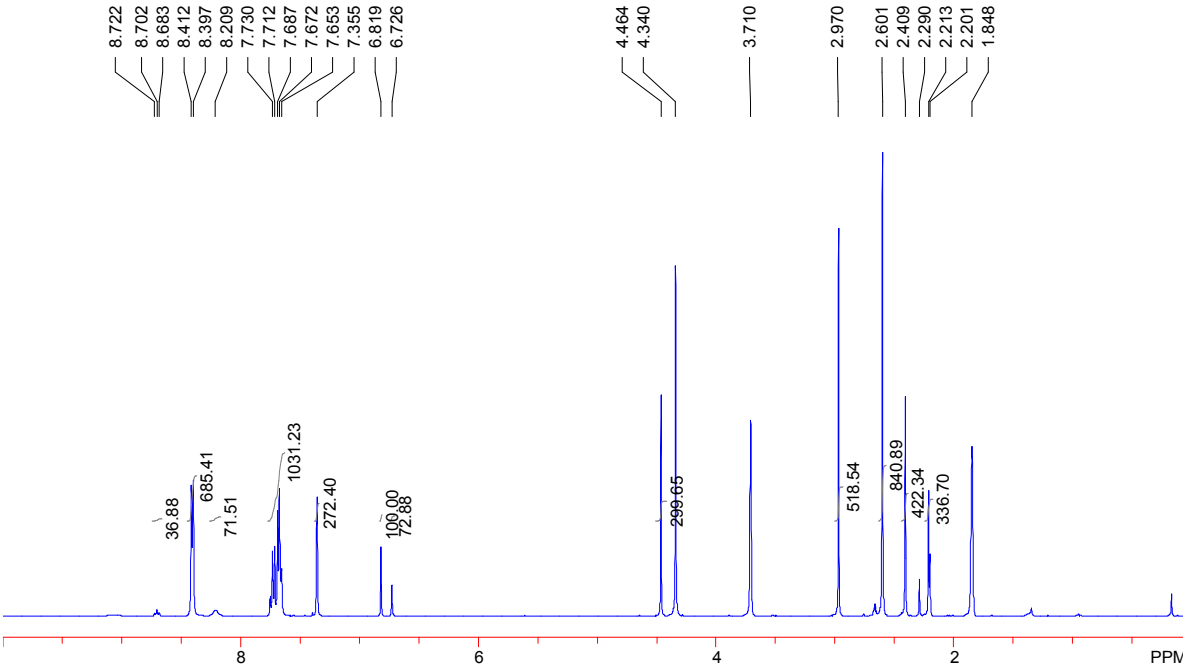


Figure S 10. ^{1}H NMR of $MesReO_3$ + PyNO in 5:1 THF-D_8:D_2O at T = 24 h at 75 °C showing formation of 2,4,6-trimethylphenol: δ 8.72 and 8.20 (pyridine); 8.41 and 7.07 (pyridine N-oxide); 7.35, 2.60, and 2.29 ($MesReO_3$); 6.72, 2.21 and 2.20 (2,4,6-trimethylphenol); 3.71 and 1.84 (residual protio THF); 6.81 and 4.46 (1,3,5-trimethoxybenzene from external standard); 4.34 (residual protio H_2O in solution); 2.97 (residual H_2O in external standard).

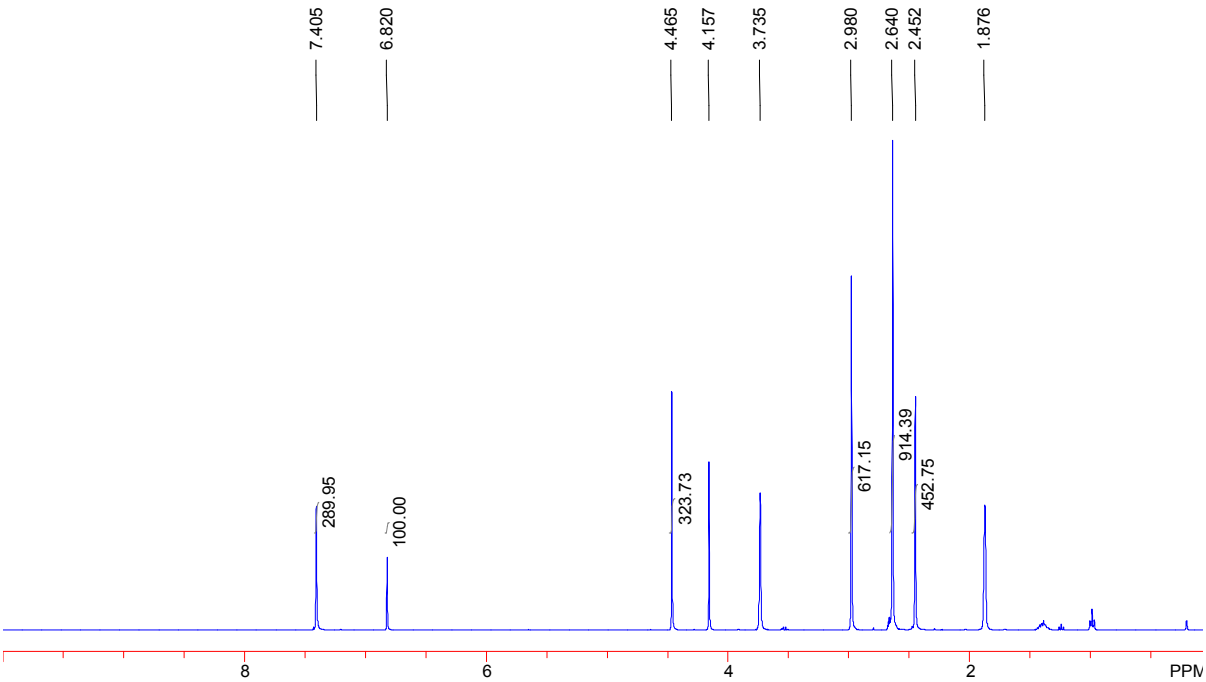


Figure S 11. ^{1}H NMR of $MesReO_3$ + 3eq DMSO-D_6 in 5:1 THF-D_8:D_2O at T = 0 h: δ 7.40, 2.64, and 2.45 ($MesReO_3$); 3.73 and 1.87 (residual protio THF); 6.82 and 4.46 (1,3,5-trimethoxybenzene from external standard); 4.15 (residual protio H_2O in solution); 2.98 (residual H_2O in external standard).

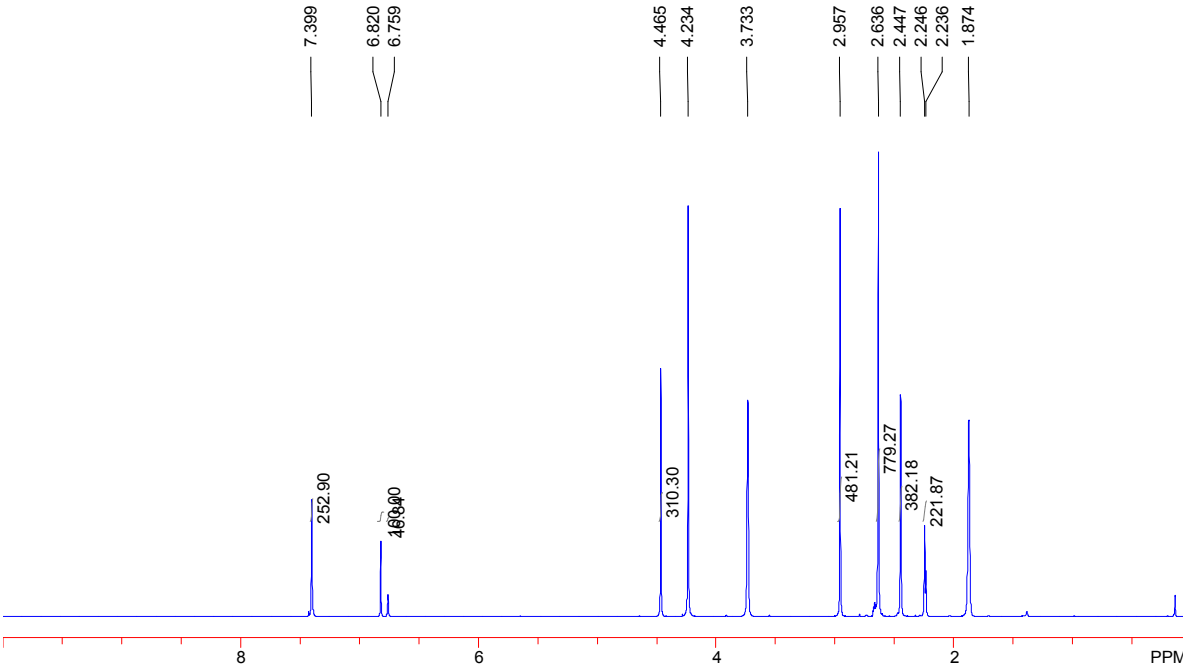


Figure S 12. ^{1}H NMR of $MesReO_3$ + 3eq DMSO-D_6 in 5:1 THF-D_8:D_2O at T = 72 h at 100 °C showing formation of 2,4,6-trimethylphenol: δ 7.39, 2.63, and 2.44 ($MesReO_3$); 6.75, 2.24 and 2.23 (2,4,6-trimethylphenol); 3.73 and 1.87 (residual protio THF); 6.82 and 4.46 (1,3,5-trimethoxybenzene from external standard); 4.23 (residual protio H_2O in solution); 2.98 (residual H_2O in external standard).

^{18}O Labeling Study: In an argon filled glovebox with the light off, a screw cap 4 mL vial with PTFE septa and containing a magnetic stir bar was loaded with ~15 μmol of respective ReArylO$_3$. To this solid, 0.6 mL of a 5:1 solution of THF-D$_8$:D$_2$^{18}O was added to the vial. Then, 3 eq. of a 3 % solution of H$_2$^{18}O$_2$ in H$_2$^{18}O was added to the vial and the reaction was stirred for 1 h at RT. The reaction was then analyzed by GC-MS. Formation of ^{18}O labeled was confirmed by comparison to authentic ^{16}O samples of 2,4,6-trimethylphenol as represented by the n+2 shift in the mass spectrum as compared to authentic samples. Retention time of authentic sample and product from reaction on RTX-5 column was 7.2 minutes.

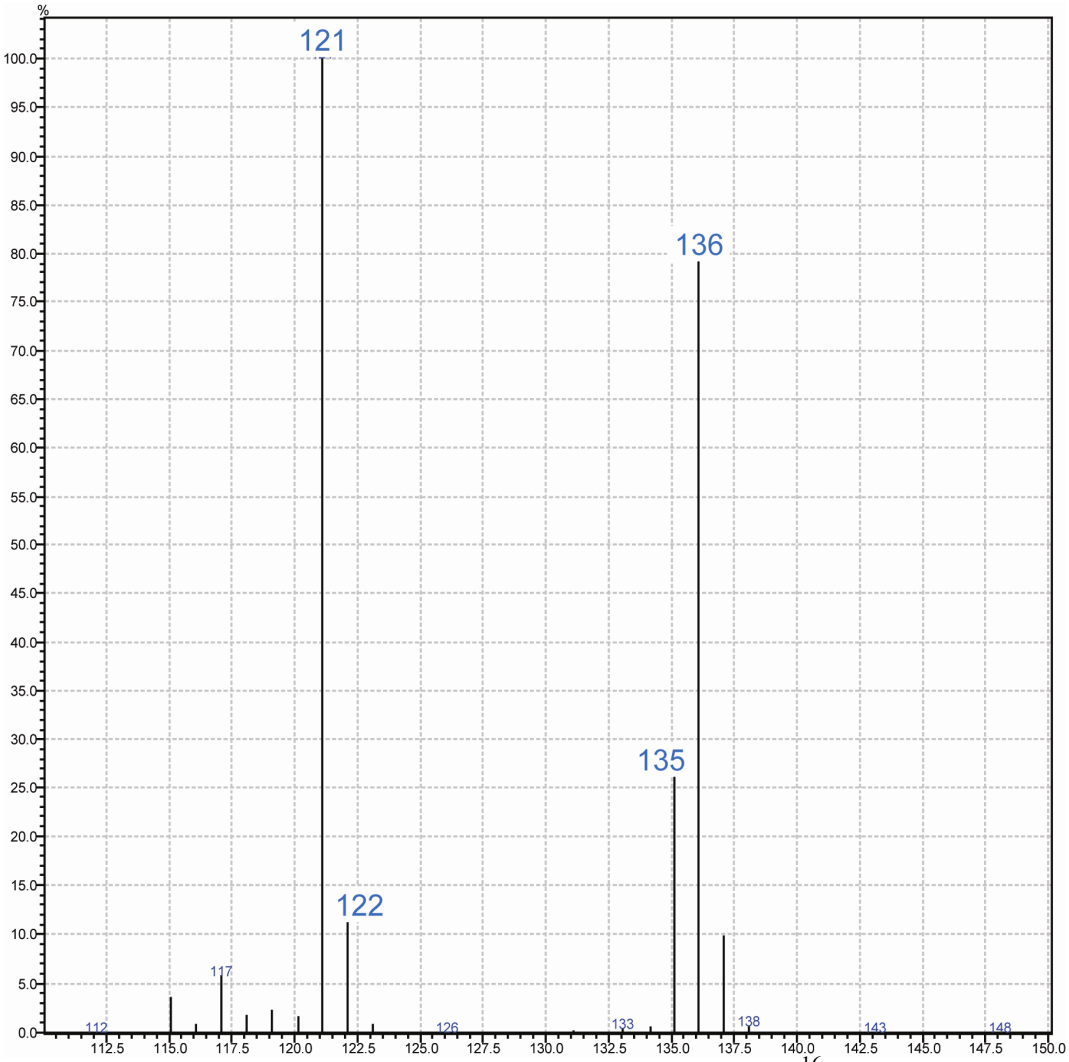


Figure S 13. GC-MS fragmentation pattern of authentic ^{16}O labeled 2,4,6-trimethylphenol (absolute intensity vs m/z).

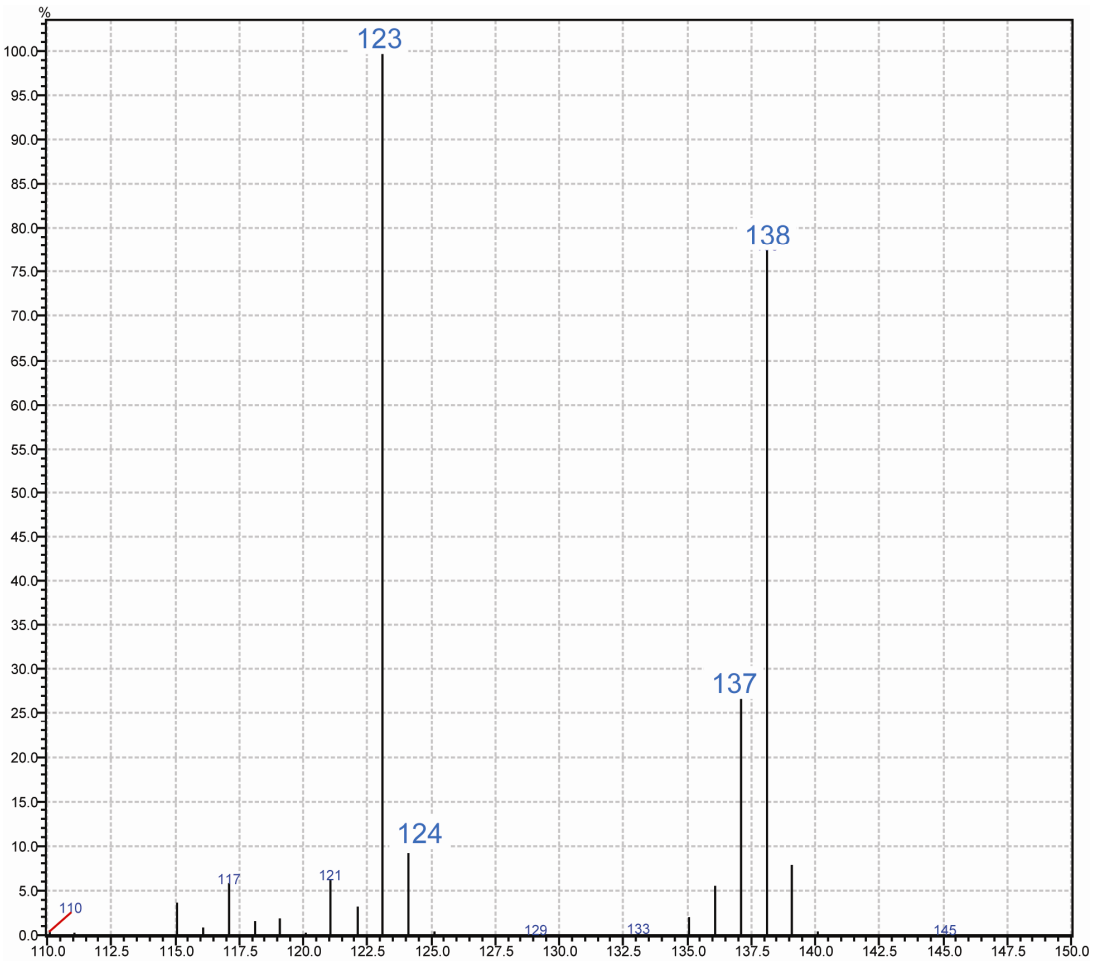


Figure S 14. GC-MS fragmentation pattern of the product from the reaction of $MesReO_3$ and $H_2{}^{18}O_2$ in 5:1 THF:$H_2{}^{18}O$ showing ^{18}O-labeled 2,4,6-trimethylphenol (absolute intensity vs m/z).

Alkyl Versus Aryl Competition Study: A screw cap NMR tube with a PTFE septa was loaded with 0.6 mL of a 5:1 THF-D_8:D_2O solution containing $MesReO_3$ (33 mM) and MTO (33 mM) and an external standard containing 1,3,5-trimethoxybenzene in CD_3CN. To the mixture of MTO and $MesReO_3$, 0.1 eq of a 1.28 M solution of H_2O_2 in D_2O was added by syringe and the tube shaken and allowed to sit for 1 h at RT. The reaction was monitored by ^1H NMR before and after the reaction.

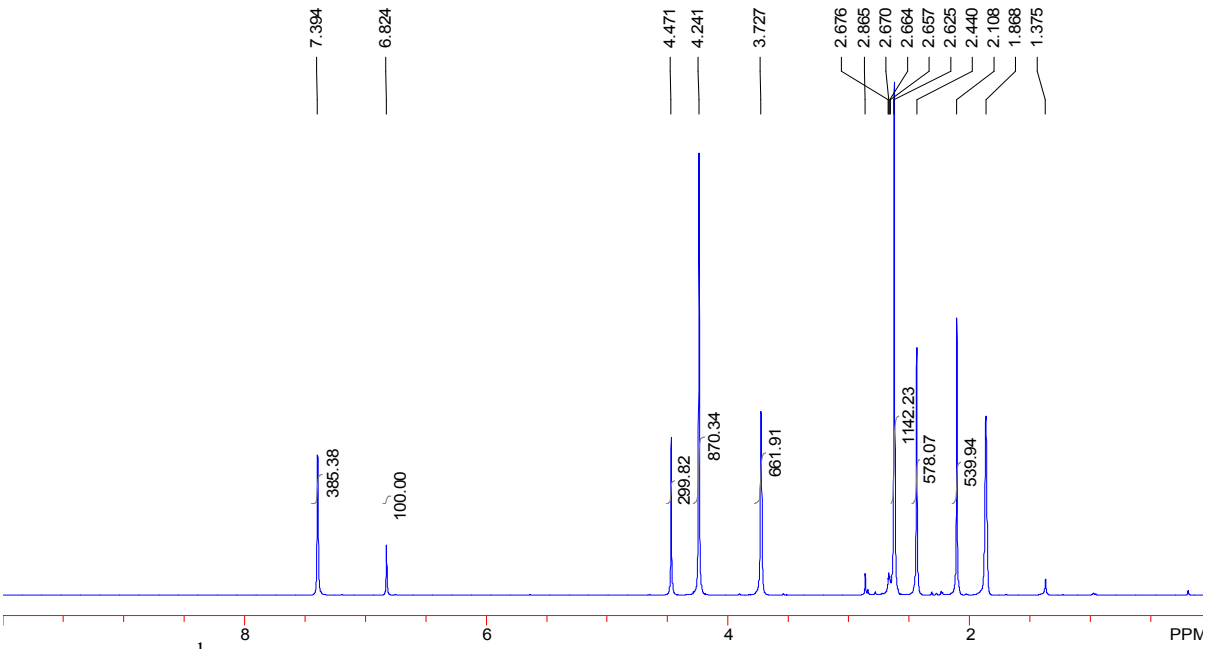


Figure S 15. ^{1}H NMR of $MesReO_3$ and MTO in 5:1 THF-D_8:D_2O at T = 1 h with 1,3,5-trimethoxybenzene in CD_3CN external standard: δ 7.39, 2.62, and 2.44 ($MesReO_3$), 6.82 and 4.47 (1,3,5-trimethoxybenzene), 4.24 (residual protio H_2O in solution), 3.72 and 1.86 (residual protio THF), and 2.10 (MTO).

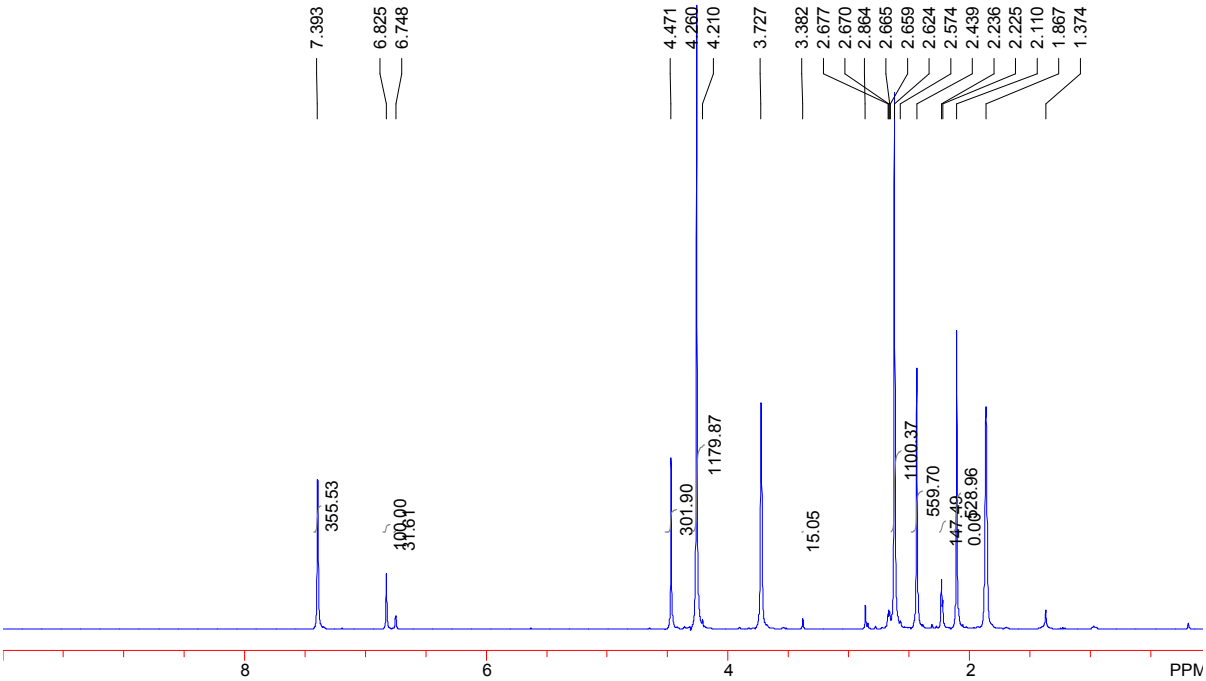


Figure S 16. ^{1}H NMR of $MesReO_3$ and MTO in 5:1 THF-D_8:D_2O at T = 1 h with 1,3,5-trimethoxybenzene in CD_3CN external standard: δ 7.39, 2.57, and 2.43 ($MesReO_3$), 6.82 and 4.47 (1,3,5-trimethoxybenzene), 6.74 2.23, and 2.22 (2,4,6-trimethylphenol), 3.72 and 1.86 (residual protio THF), 3.38 (MeOH) and 2.11 (MTO).

Computational details

The geometry optimizations and zero-point vibrational energy (ZPVE) were carried out using the B3LYP functional[5] with the 6-31G**basis set[6] for all atoms except Re. For Re the first four shells of core electrons were described by the Los Alamos angular momentum projected effective core potential (ECP) using the double-ζ contraction of valence functions[7] (denoted as LACVP**). In order to obtain more accurate electronic energy, single-point energy calculations based on the M06 functional, and using a larger basis set were performed, where Re was described with the triple-ζ contraction of valence functions augmented with two f functions[8] and the core electrons were described by the same ECP, and the other atoms were described with the 6-311++G** basis set.[9]

Solvation energies were calculated using the Poisson-Boltzmann self-consistent polarizable continuum method[10] implemented in Jaguar[11] to represent water (dielectric constant = 80.37 and effective radius = 1.40 Å), THF (dielectric constant = 7.6 and effective radius = 2.52 Å), and DMSO (dielectric constant = 47.25 and effective radius = 2.41 Å). The solvation calculations used the B3LYP/LACVP** level of theory and the gas-phase optimized structures.

All energies discussed in this work are Gibbs free energies. For organometallic species these are calculated as:

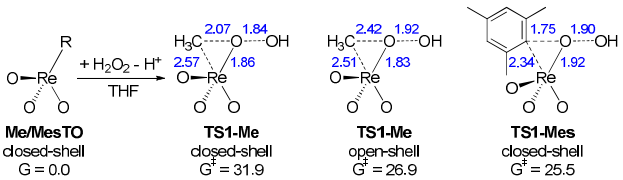
$$G_{298K} = E_{elec} + G_{solv} + ZPVE + \sum_{\nu} \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{n}{2}kT - T(S_{vib} + S_{rot} + S_{trans}),$$

where n = 12 accounts for the potential and kinetic energies of the translational and rotational modes and T = 298K. The values of (S_{rot} + S_{trans}) for each Re intermediate were assumed to cancel.

The free energy of $H_2O_{2(aq)}$, $HOO^-_{(aq)}$, and $H^+_{(aq)}$ at pH = 7 in aqueous solution were calculated by adding the computed ideal gas phase Gibbs free energy and the experimentally measured solvation free energy $\Delta G(1atm \rightarrow 1M)$[12] and correcting for concentration via $G = G^\circ + kT\ln(C/C^\circ)$.

For the comparison of methyltrioxorhenium and mesityltrioxorhenium oxidation rates in 5:1 THF:H_2O, we used the continuum solvent parameters for THF. We used the aqueous free energies of H_2O and H_2O_2. For the free energy of the proton in this solvent mixture, we added 5 kcal/mol to the pH = 7 aqueous free energy, using the free energies for the proton in methanol and water recommended by Truhlar (Kelly, C. P.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2007**, *111*, 408.) as a guide.

Using density functional theory (DFT) and the Poisson-Boltzmann polarizable continuum solvation model representing THF, we calculated the Gibbs free energy barriers $\Delta G^\ddagger$ of $MesReO_3$ and CH_3ReO_3 oxidation by the BV path using H_2O_2 to be 25.5 and 26.9 kcal/mol, respectively, consistent with the competition experiment ($\Delta\Delta G^\ddagger$ ~1 kcal/mol for ~4:1 ratio of rates). Surprisingly, we found that the nature of the two transition states are different than those previously reported. Hallmark long bond distances to the methyl fragment in its transition state suggested significant diradical character develops, and indeed a transition state with an open-shell singlet wavefunction (Scheme S 1) is more stable than the restricted-orbital version ($\Delta G^\ddagger$ = 31.9 kcal/mol). Attempts to locate an open-shell wavefunction for the mesityl transition state collapsed back to the closed-shell wavefunction.



Scheme S 1. Transition states for open and closed shell wavefunctions for BV migrations of R-ReO_3 where R = Me or Mes with bond lengths shown in Å and energies in kcal/mol.

DFT X,Y,Z Coordinates

Baeyer-Villiger transition state of $CH_3ReO_3 + H_2O_2$ (closed shell singlet)

E(SCF) = -495.65713734440

C1	0.0000000000	0.0000000000	0.0000000000
O2	0.0000000000	0.0000000000	2.0682954981
O3	0.3712691168	0.0000000000	3.8686955709
Re4	1.2728460914	1.3237546804	1.7910112193
O5	2.8183139834	0.6642317596	2.1797072504
O6	0.7995229502	2.6046874834	2.8573084636
O7	1.5652022602	2.1993135300	0.3148597597
H8	-0.2069019619	0.7488126352	4.0856050391
H9	-0.6565328299	-0.8555713647	0.1268975568
H10	-0.4763916346	0.8595359312	-0.4643809280
H11	0.9381033837	-0.2640874122	-0.4871630487

Baeyer-Villiger transition state of $CH_3ReO_3 + H_2O_2$ (open-shell singlet)

E(SCF) = -495.65713734440

C1	0.0000000000	0.0000000000	0.0000000000
O2	0.0000000000	0.0000000000	2.4179726163
O3	0.2232552045	0.0000000000	4.3267551770
Re4	-1.7283103815	-0.0381981533	1.8220535884
O5	-2.3066426952	1.3778430417	1.0109621382
O6	-2.4518423914	-0.0511871040	3.4162890815
O7	-2.2432189837	-1.4811547214	1.0156502018
H8	-0.7510196768	-0.0190117686	4.4098251138
H9	0.5433072908	0.9340819659	0.0942584887
H10	0.6050566355	-0.8934596256	0.1093390436
H11	-0.7186829179	-0.0310089499	-0.8165163609

Baeyer-Villiger transition state of $MesReO_3 + H_2O_2$ (closed shell singlet)

E(SCF) = -805.18327071464

C1	0.0000000000	0.0000000000	0.0000000000
O2	0.0000000000	0.0000000000	1.7538161037
Re3	1.8854727827	0.0000000000	1.3924193621
O4	-0.5823357591	-0.0040537777	3.5622756018
O5	2.5949975814	-1.4257678529	0.7193398734
O6	2.2015985750	-0.0089377147	3.1005741562
O7	2.5932846149	1.4330398731	0.7330974743
H8	0.3177584188	-0.0099898848	3.9274316375
C9	-0.4292594604	1.2263390089	-0.5689270311
C10	-0.4320024058	-1.2284207453	-0.5641907483
C11	-1.1419787532	1.1945431394	-1.7704020069
C12	-1.1442742232	-1.2006474688	-1.7651729931
C13	-1.4885943817	-0.0037282217	-2.4025968233
H14	-1.4528824111	2.1396296847	-2.2144699786
H15	-1.4577188879	-2.1470617048	-2.2047743418
C16	-0.1843974831	2.5464921777	0.1173399616
H17	0.8780825950	2.8090192253	0.1079163379
H18	-0.7531331024	3.3459473890	-0.3689679483
H19	-0.4891886156	2.4816302633	1.1670477304
C20	-0.1901749204	-2.5455653173	0.1290363774
H21	-0.7596947010	-3.3464988277	-0.3539078380
H22	0.8719264921	-2.8098987579	0.1217527639
H23	-0.4960368078	-2.4745183799	1.1780633584
C24	-2.2300107391	-0.0076069213	-3.7190567338
H25	-1.5424350937	-0.0761161162	-4.5741405210
H26	-2.9156493127	-0.8597206221	-3.7915046337
H27	-2.8169050519	0.9081434549	-3.8509928999

1

E(SCF) = -536.30353330799

Re1	-1.3549546430	0.5967862190	-0.0486127469
C2	-0.6294675375	1.5585073653	1.6147895832
C3	-0.4161762358	0.8404435943	2.8069626132
C4	-0.3921318893	2.9459308489	1.5831692944
C5	0.0163418726	1.5075375863	3.9511859041
H6	-0.5814519342	-0.2317425928	2.8387940244
C7	0.0406050892	3.6023521851	2.7336749798
H8	-0.5390468039	3.5068028833	0.6657978785
C9	0.2425426910	2.8854935096	3.9152845556
H10	0.1820139264	0.9504775791	4.8683662803
H11	0.2252801466	4.6719748374	2.7054170697
H12	0.5839814053	3.4006276760	4.8084086414
O13	-3.0599234774	0.6561324673	0.0895327575
O14	-0.7746023322	1.4901423579	-1.3859146248
O15	-0.7470962838	-0.9988200355	0.0408513499

3

E(SCF) = -687.32967030605

C1	0.0000000000	0.0000000000	0.0000000000
O2	0.0000000000	0.0000000000	2.4489965402
Re3	1.7186711959	0.0000000000	1.3977868929
O4	0.1744386475	-0.1081484009	3.8903860997
O5	2.2614073122	-1.6226363513	1.2261652474
O6	2.3581698411	0.6735425408	2.9016221632
O7	2.4841808388	0.9865401167	0.1978095190
H8	1.0713851142	0.3060841955	3.9582949106
C9	-0.0187401267	0.8487475277	-1.1178061717
C10	-1.0714828141	-0.8983113232	0.1475885806
C11	-1.0626646216	0.8099880606	-2.0477527582
H12	0.8062275942	1.5397841698	-1.2633406996
C13	-2.1086195494	-0.9536474494	-0.7860054166
H14	-1.0950558368	-1.5541945701	1.0107182035
C15	-2.1130525729	-0.0935899623	-1.8865170737
H16	-1.0516741497	1.4854089640	-2.9019103090
H17	-2.9198805902	-1.6666069032	-0.6503602082
H18	-2.9250788189	-0.1297943574	-2.6105022959

4

E(SCF) = -536.27445341170

Re1	-1.4168639046	0.6020143795	-0.0389632405
O2	-3.0579414853	0.8191353524	0.3792991945
O3	-1.0858839754	1.3527489171	-1.5367349913
O4	-1.0548995785	-1.0624731394	-0.1603932096
O5	-0.3869526783	1.3836411001	1.3097628156
C6	1.0068286739	1.4401146709	1.3787843613
C7	1.6896918355	0.4222735437	2.0411511757
C8	1.6652846515	2.5356740336	0.8244441053
C9	3.0775764023	0.5103326264	2.1469164801
H10	1.1387323931	-0.4147087242	2.4579384427
C11	3.0533687647	2.6069967387	0.9399943956
H12	1.0958599752	3.3066872274	0.3154127581
C13	3.7598637380	1.5988441763	1.5993248507
H14	3.6240241055	-0.2757785309	2.6590139598
H15	3.5809291720	3.4540047653	0.5121058736
H16	4.8403002469	1.6605312279	1.6848090060

TS1

E(SCF) = -687.29776961317

C1	0.0000000000	0.0000000000	0.0000000000
O2	0.0000000000	0.0000000000	1.7024756628
Re3	1.8791473075	0.0000000000	1.3624945288
O4	-0.5967968280	-0.0001821814	3.5367018570
O5	2.5420221033	-1.4376303879	0.6709978067
O6	2.2196214011	0.0002368674	3.0659565588
O7	2.5420364278	1.4374646549	0.6706580279
H8	0.3048084293	0.0001756480	3.8983782700
C9	-0.3938777703	1.2136427285	-0.5935719664
C10	-0.3942593542	-1.2136330587	-0.5933521407
C11	-1.1348468198	1.2081893442	-1.7720742296
H12	-0.0940596913	2.1498163608	-0.1330924449
C13	-1.1352424692	-1.2081620304	-1.7718456854
H14	-0.0947590203	-2.1498063989	-0.1326650326
C15	-1.5107266075	0.0000203538	-2.3701729320

TS2

E(SCF) = -687.81203226884

C1	-0.0295898057	-0.0099152595	0.0338481474
O2	0.0079406467	0.1283511091	2.0108439785
Re3	1.7897081350	-0.0492280164	1.2147429310
O4	0.1032296095	0.2928008817	3.7839573429
O5	2.3350377670	-1.5395250998	0.5830933258
O6	2.2841274391	-0.0161406322	2.9586384630
O7	2.5176431118	1.2923652946	0.4508460510
H8	1.3214716258	0.1209406710	3.5917812553
C9	-0.4754617313	1.2128374910	-0.4959748771
C10	-0.6025005655	-1.2227985793	-0.3851930324
C11	-1.4427370118	1.2114705814	-1.4964762012
H12	-0.0512374770	2.1460042374	-0.1419898885
C13	-1.5713742175	-1.2111204438	-1.3839089383
H14	-0.2691903299	-2.1608133251	0.0454661785
C15	-1.9891849151	0.0027741347	-1.9395006991
H16	-1.7756267349	2.1511482075	-1.9267458345
H17	-2.0026343012	-2.1461354857	-1.7286782667
H18	-2.7479048215	0.0067912575	-2.7168823806
H19	-0.3180097147	-0.5636261121	3.9586297897

TS3

E(SCF) = -611.36368132885

C1	0.0000000000	0.0000000000	0.0000000000
O2	0.0000000000	0.0000000000	1.9400935377
Re3	1.7216552862	0.0000000000	1.2316602890
O4	1.6306085011	-0.0002647038	3.0632056233
O5	2.5070992121	-1.4247660334	0.6985146027
O6	2.5076052237	1.4245968755	0.6987295580
C7	-0.5994700356	1.2301486320	-0.3993567403
C8	-2.3140828368	0.0001500595	-1.5684229773
C9	-1.7453338203	1.2216048294	-1.1774446169
C10	-1.7432431358	-1.2214196222	-1.1805188627
C11	-0.5975118240	-1.2301225114	-0.4023807258
H12	-0.1514199556	2.1667080664	-0.0836860506
H13	-0.1478468945	-2.1667349853	-0.0891819000
H14	-2.2076628131	2.1563607095	-1.4785479675
H15	-2.2039641419	-2.1561198120	-1.4842463590
H16	-3.2188119506	0.0001390051	-2.1699680929

TS4

E(SCF) = -686.59214358126

C1	0.0000000000	0.0000000000	0.0000000000
O2	0.0000000000	0.0000000000	1.8052056345
Re3	1.7636189962	0.0000000000	1.1244357080
O4	2.6325856014	0.0011402178	-0.5789090050
O5	3.8004672575	0.0006119491	0.2659444920
C6	-0.5573930002	1.2129230759	-0.5391349775
C7	-1.6729377305	1.1997632583	-1.3656874960
C8	-2.2733747027	0.0004720536	-1.7885789542
C9	-1.6748314581	-1.1991617767	-1.3636726471
C10	-0.5592971403	-1.2128515484	-0.5372973635
O11	2.1622804975	1.5771718027	1.7789434972
O12	2.1622807304	-1.5779130891	1.7770577357
H13	-0.1112203376	-2.1611821416	-0.2530704792
H14	-0.1076957149	2.1610266012	-0.2565173190
H15	-2.0798435218	-2.1537716351	-1.7128248384
H16	-2.0762095876	2.1544951349	-1.7165314238
H17	-3.1354666658	0.0006627776	-2.4554102810

TS5

E(SCF) = -611.35160194506

C1	0.0000000000	0.0000000000	0.0000000000
O2	0.0000000000	0.0000000000	1.8057928557
Re3	1.7365327845	0.0000000000	1.4573618195
O4	2.6325937746	1.5165944994	0.6885922092
O5	2.8450443830	1.3942391756	2.1188761263
O6	2.4814293851	-1.5125997764	1.3328161632
C7	-0.4307519901	-1.2240541284	-0.5204735465
C8	-0.3489498103	1.2263706441	-0.5720977691
C9	-1.1561070552	-1.2107630310	-1.7109734443
H10	-0.1922094140	-2.1545703901	-0.0178708926
C11	-1.0748870404	1.2128892787	-1.7601615948
H12	-0.0347518860	2.1590211533	-0.1164439969
C13	-1.4750825621	0.0002886681	-2.3318063798
H14	-1.4819174320	-2.1509969512	-2.1455904030
H15	-1.3323663926	2.1537810710	-2.2367669279
H16	-2.0488501656	0.0008583137	-3.2532334114

TS6

E(SCF) = -536.22723533022

C1	0.0000000000	0.0000000000	0.0000000000
O2	0.0000000000	0.0000000000	1.8358705112
Re3	1.7342190835	0.0000000000	1.4399697392
C4	-0.4337538027	1.2252524612	-0.5223914937
C5	-0.4338703323	-1.2252063985	-0.5223941359
C6	-1.2509483109	1.2129173966	-1.6501195879
H7	-0.1306934439	2.1597886190	-0.0634848417
C8	-1.2510526893	-1.2127688068	-1.6501319358
H9	-0.1309121801	-2.1597826400	-0.0635003663
C10	-1.6572037802	0.0000966236	-2.2157276804
H11	-1.5818257407	2.1539456187	-2.0789339842
H12	-1.5820128816	-2.1537618715	-2.0789629531
H13	-2.3071718914	0.0001277408	-3.0853273431
O14	2.6182207566	-1.4597250297	1.4540608504
O15	2.6180991214	1.4597857364	1.4538914254

H_2O_2

E(SCF) = -151.52291874024

O1	-0.7277424041	-0.0205585884	-0.0291836785
H2	-0.9158325161	0.7940775104	0.4631661556
O3	0.7277424041	0.0205585884	-0.0291836785
H4	0.9158325161	-0.7940775104	0.4631661556

H_2O

E(SCF) = -76.41823803483

O1	0.0000000000	0.0000000000	-0.0665107418
H2	0.0000000000	0.7601703783	0.5277868689
H3	0.0000000000	-0.7601703783	0.5277868689

DMSO-1

E(SCF) = -1089.47187806404

C1	0.2558343176	0.1436505556	-0.1469799259
O2	-0.1935578339	-0.9777428461	2.4168809293
Re3	1.8092432649	0.0162678752	1.2404613381
O4	2.3313649587	-1.5861383671	1.5532346055
O5	1.6155857458	1.0344363465	2.6199280303
O6	3.0034629412	0.7541470999	0.2663364979
C7	0.1150500311	1.3314712902	-0.8882500700
C8	-0.6339754937	-0.9182010907	-0.3834872208
C9	-0.9072571262	1.4599015401	-1.8281968465
H10	0.8109542551	2.1521993016	-0.7429561765
C11	-1.6390666009	-0.7920606000	-1.3422217361
H12	-0.5444669401	-1.8351639762	0.1860569637
C13	-1.7836655846	0.3975132397	-2.0586060553
H14	-1.0094792168	2.3845801333	-2.3891303917
H15	-2.3143422469	-1.6233859175	-1.5249897443
H16	-2.5722633451	0.4942861977	-2.7995897526
S17	0.0956135549	-1.1700734016	3.9201977018
C18	-1.0299597858	-2.5130979027	4.4153227909
H19	-0.9914634503	-2.6351435675	5.5011050098
H20	-2.0429916023	-2.2798691896	4.0802896318
H21	-0.6719340319	-3.4206700951	3.9264949121
C22	-0.7415771232	0.2082041107	4.7672383924
H23	-0.1902489544	1.1048392989	4.4815379255
H24	-1.7780568609	0.2713864982	4.4279792308
H25	-0.6855928762	0.0553093245	5.8485777216

DMSO-1,2-TS

E(SCF) = -1089.41362354543

C1	0.0000000000	0.0000000000	0.0000000000
O2	0.0000000000	0.0000000000	1.9738303026
S3	0.1077755901	0.0000000000	4.0067891166
Re4	-1.8182560582	0.2866415257	1.3130305471
O5	-2.2425962574	1.7713858256	0.5659188170
O6	-2.2594290159	0.3950794182	3.0019744376
O7	-2.6454831061	-1.0633948399	0.6506028342
C8	0.2542907978	-1.2675281409	-0.5362015627
C9	0.6202388106	1.1385048810	-0.5275374157
C10	1.0728064852	-1.3818373397	-1.6593505991
H11	-0.2145114262	-2.1466225364	-0.1059004334
C12	1.4355612400	1.0142470492	-1.6513098172
H13	0.4335017579	2.1136458102	-0.0897607646
C14	1.6626125972	-0.2436339696	-2.2170135545
H15	1.2494172256	-2.3589206127	-2.1003497485
H16	1.8927672089	1.8990981632	-2.0854509185
H17	2.3005277415	-0.3370392895	-3.0912834237
C18	1.8513678857	-0.4944308130	3.8641148573
H19	2.2405054305	-0.7549771728	4.8514416473
H20	1.9473633035	-1.3316327359	3.1710010403
H21	2.3933773746	0.3660106253	3.4690945955
C22	-0.6301379054	-1.5875717441	4.4886669727
H23	-1.6882505689	-1.3935392884	4.6579623023
H24	-0.5128644962	-2.3041014336	3.6721297238
H25	-0.1450406741	-1.9580362135	5.3953948024

DMSO-2

E(SCF) = -1089.51919555389

C1	0.0000000000	0.0000000000	0.0000000000
O2	0.0000000000	0.0000000000	1.3843388477
S3	0.9229135623	0.0000000000	4.2770761568
Re4	-1.5126070920	0.1234300063	2.5439595186
O5	-1.6614500935	1.5543814413	3.4691448037
O6	-1.8586812605	-1.2733893205	3.4802813670
O7	-2.7236278910	0.2038491293	1.3420546388
C8	0.2478992436	-1.1980203133	-0.6721059628
C9	-0.2051506116	1.1898005459	-0.6997000036
C10	0.2799618321	-1.1991925286	-2.0667633362
H11	0.4017750325	-2.1097138666	-0.1011431546
C12	-0.1734946813	1.1726047626	-2.0939576825
H13	-0.3941954344	2.1074334119	-0.1518812201
C14	0.0677642274	-0.0182891329	-2.7809785459
H15	0.4638625187	-2.1297126368	-2.5952477240
H16	-0.3430387855	2.0959709926	-2.6428004952
H17	0.0869581142	-0.0253955121	-3.8672156490
C18	1.8510976218	-1.3919560624	3.5538205246
H19	2.6507892602	-1.6993875212	4.2308978517
H20	1.1852930708	-2.2351002584	3.3496091438
H21	2.2767379854	-1.0310014014	2.6147318910
C22	0.2055842097	-0.8141048743	5.7423749647
H23	-0.4064485670	-0.0683691668	6.2522421913
H24	-0.4325994363	-1.6418121172	5.4293725375
H25	0.9999185196	-1.1581793629	6.4101525673

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